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ABSTRACT

Four possible theoretical explanations are proposed of the experimentally observed differences between piston-supported overdriven detonation waves and self-sustaining converging detonation waves. The simplest and most probable explanation is that additional exothermic reactions, possibly involving solid carbon states, occur in piston-supported waves where the high pressures and temperatures are maintained for relatively long times. These slower reactions can not affect self-sustaining waves, because they occur in the following rarefaction waves and thus can not communicate with the reaction zone. Another possible explanation involves the attainment of frozen

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rather than equilibrium product states in the small scale overdriven wave experiments.Two other possibilities are also mentioned which involve the relative compressibilities and the energy release rates of unreacted explosives at extremely high pressures. Areas of further experimental and theoretical research are identified.

INTRODUCTION

Recent experiments[1] on piston-supported overdriven detonation waves in several heterogeneous solid high explosives have confirmed previous data of Kineke and West,[2] which showed that the states measured in these experiments do not correspond to the states predicted by the standard Jones-Wilkins-Lee (JWL) equations of state fitted to Chapman-Jouguet (CJ) state and cylinder test data.[3] The situation is shown graphically in Fig. 1-3 for the pressure-specific volume, pressure-particle velocity, and shock velocity-particle velocity planes, respectively. Several equations of state[4] have been formulated in attempts to match this overdriven data and the lower pressure metal acceleration (cylinder test) data. All of these equations of state require the use of a lower CJ pressure than the normal CJ value. This lower P_{CJ} state is labeled the frozen equilibrium sonic state in Figs. 1 and 2. In the case of PBX-9404, this lower P_{CJ} value is approximately 33-34 GPa while the standard value is 37 GPa. Differences of approximately this magnitude are required for most of the explosives studied.[1,2] However, the PETN experimental data can be fitted above and below CJ with one value of 31.6 GPa,[4] and the available TNT data[2] appears to agree with the standard JWL equation of state up to pressures well above CJ and then deviate in the usual manner.

The main problem develops when these low CJ pressure equations of state are used to calculate metal acceleration and converging detonation wave propagation data. The ignition and growth reactive flow model which contains the standard JWL reaction product equations of state and the usual P_{CJ} values has accurately calculated a great deal of one- and two-dimensional shock initiation, detonation wave propagation, and metal acceleration data[5-13] on heterogeneous solid explosives and propellants. One example of the ability of the reactive flow model with the standard JWL equation of state to accurately calculate recent metal acceleration data is shown in Fig. 4 for 17 mm of PBX-9404 driving a 0.5 mm copper plate.[11] Also shown in Fig. 4 is the corresponding reactive flow calculation for a P_{CJ} = 34 GPa reaction product JWL equation of state. The equation of state and reaction rate parameters used in these calculations are listed in Table I. Even with the reactive flow model, the P_{CJ} = 34 GPa equation of state does not deliver enough energy to the thin metal plate. In the case of self-sustaining converging detonation, Tarver and Urtiew[10] demonstrated that the ignition and growth reactive flow model for PBX-9404 accurately calculates the experimental data of Cheret et. al.[14] for detonating PBX-9404 spherically converging from 14 cm and 15 cm outer radii to 1.5 cm inner radius. In the 15 cm outer radius experiment, the effect of the initiation system is negligible after 1 cm of detonation, and both sets of Cheret's pin data recorded 13.3 μs for propagation from 14 cm to 1.5 cm. The reactive flow calculations with the standard P_{CJ} = 37 GPa reaction product equation of state also yield 13.3 μs for this distance. Reactive flow calculations using the P_{CJ} = 34 GPa reaction product equation of state predict a time fo 13.0 μs for the convergence from 14 cm to 1.5 cm in this 15 cm outer radius experiment. Thus the low P_{CJ} equation of state yields too fast a convergence, because it predicts higher shock velocities and pressures than the standard higher P_{CJ} equation of state, as shown in Figs. 1-3.

Therefore there appears to be a dilemma in which a single reaction product equation of state can not calculate all four types of experimental data: CJ and reaction product expansion; metal acceleration; converging detonation; and overdriven detonation. However, there may be fundamental differences between the self-sustaining CJ and converging detonation waves for which metal acceleration data is measured and the piston-supported overdriven detonation waves which are currently being measured. Four possible theoretical explanations of these differences are discussed in detail in the next section.

THEORETICAL EXPLANATIONS OF THE DIFFERENCE BETWEEN SELF-SUSTAINING AND PISTON-SUPPORTED DETONATION WAVES

1. Additional Exothermicity in Piston-Supported Waves

The simplest and most likely explanation of the differences between the piston-supported overdriven detonation data and the standard JWL product equation of state which appears to describe self-sustaining, converging detonation states is illustrated by points P1 and P2 in Figs. 1 and 2. For a detonation wave with velocity D'>D, the state point moves along the Rayleigh line from S', the unreacted von Neumann spike state, to point P1 as the chemical energy release occurs. In a self-sustaining detonation wave the product state CJ or P1 (or perhaps CJ' in Fig. 5 in the case of converging detonation waves[10]) is followed by a rarefaction or Taylor wave in which the pressure and temperature rapidly decrease. In a piston-supported wave the pressure and temperature at P1 are kept high for a relatively long time by the motion of the piston. Perhaps additional exothermic reactions occur in this high pressure region to cause the pressure to decrease from P1 to P2 in Figs. 1 and 2. The final product state P2 measured in a piston-supported overdriven experiment would therefore be different from the corresponding state P1 or CJ' measured in a self-sustaining, converging detonation experiment.

This postulated additional exothermic process that occurs in a piston-supported wave may be related to the fascinating problem of the formation of solid carbon in detonation waves that has been addressed by Hayes,[15] Mader,[16] Ree[17] and many others. The question of whether solid carbon exists in the short chain, long chain, graphite, and/or diamond forms and the times requires for formation of the various forms is quite complex. However, if the time required to reach a more stable form of solid carbon at high pressures and temperatures is long relative to the usual reaction zone length of a self-sustaining detonation wave but short relative to the time available in a piston-supported experiment, then the exothermic process of forming a more stable form of solid carbon could easily account for the difference in energy between states P1 and P2. The idea that solid carbon is involved fits well with the PETN data which does not exhibit the overdriven versus self-sustaining effect, because PETN is oxygen balanced and forms very little solid carbon when it detonates relative to the other explosives investigated.[1,2] At first glance the theory seems to disagree with the TNT data,[2] since TNT makes a great deal of carbon and the overdriven and standard JWL states agree near the CJ point.

However, TNT has a relatively low CJ pressure, and the stable carbon formation reaction may occur only at very high pressures and temperatures well above TNT's P_{CJ}. The higher pressure TNT piston-supported overdriven detonation data does deviate from the standard JWL equation of state in the correct direction so perhaps TNT still fits this simple idea about carbon formation. Perhaps it is not only solid carbon formation but other high pressure, high temperature exothermic processes that cause the experimental discrepancy. Further experimental and especially theoretical research is needed to explore all the possibilities and quantify the quantities of mass and energy involved in this postulated secondary exothermic process that may occur in piston-supported overdriven detonations but not in self-sustaining detonations.

2. Frozen Versus Equilibrium Product States

The positions of the curves fit to the piston-supported overdriven detonation data relative to the standard JWL equation of state in Figs. 1-3 are at first glance very reminiscent of the debate in the 1950's concerning the frozen versus equilibrium sound velocities for steady state detonation waves. This controversy is fully discussed in the classical text of Fickett and Davis.[18] The question was eventually answered by Wood and Salsburg,[19] who showed that initially the reaction products would be described by the frozen equilibrium sonic states shown in Figs. 1 and 2, but that eventually for steady-state, self-sustaining detonation waves changes in the chemical equilibrium due to reversible reactions within the reaction products cause a gradual shift to the equilibrium CJ sound velocity. Overdriven detonations were not investigated, but the presence of the rarefaction or Taylor wave was essential to Wood and Salsburg's analysis.[19] The notion of frozen versus equilibrium sound velocity led to a possible explanation of the overdriven detonation data. Perhaps the states attained in these short duration piston-supported overdriven detonation experiments correspond to frozen reaction product states, while the states attained by self-sustaining detonation waves correspond to equilibrium reaction product states that lie close to the standard JWL equation of state predictions. All of the overdriven experiments to date have used very small explosive samples (a few millimeters of detonation transit) and thus the final state of the reaction products may not have been attained if equilibration has not been completed.

The situation is illustrated in the pressure-distance diagrams of Fig. 6 for piston-supported and self-sustaining CJ and overdriven detonation waves. For CJ detonation, the situation is quite simple: there is either a piston moving with velocity u_{CJ} or a Taylor wave following the CJ sonic state in the self-sustaining case. The distribution of energy and the work done by the various mechanical and chemical processes in these two cases has been derived by Cowperthwaite and Adams.[20] For overdriven detonations the situation is more complex. In the case of piston-supported waves, the early time record should approach Fig. 6.2(a) with a nearly constant pressure state between the piston face and the end of the reaction zone. However, at later times reequilibration in the products between the piston and the reaction zone could lead to a structure like that in Fig. 6.2(b) with frozen and equilibrium sonic states. The stability of such a structure and the constancy of the shock front velocity for large propagation distances are interesting questions. Larger scale piston-supported overdriven detonation experiments are currently being planned[21] which may provide some answers to these questions. In the case of self-sustaining converging detonations, a Taylor wave is obviously present but the structure of the rear of the reaction zone is unknown. As more fully discussed by Tarver and Urtiew,[10] the state attained after reaction in a converging detonation with velocity D'>D can lie anywhere between points P1 and CJ' in the pressure-specific volume plane shown in Fig. 5. If states like P1 are attained, there will be additional structure to the converging wave in the early expansion region behind the reaction zone, as shown in Fig. 6.2. However, the presence of the Taylor wave allows the reversible chemical reactions to occur, which in turn leads to a series of equilibrium Hugoniot product states rather than frozen Hugoniot states.

Therefore the possibility of piston-supported overdriven detonation waves corresponding to frozen Hugoniot states and self-sustaining converging waves corresponding to equilibrium Hugoniot states seems quite reasonable. A quantitative estimate of the magnitude of this effect at very high pressures is difficult to make. Fickett and Davis[18] reported LJD equation of state frozen versus equilibrium CJ calculations for the products of RDX at an initial density of 1.8 g/cc. In these calculations the differences in pressure are approximately 1 GPa and in the sound velocity approximately 0.1 mm/μs. In terms of $\gamma = \partial \ln p/\partial \ln V$, the differences are approximately 0.1 (3.3 for the equilibrium state versus 3.4 for the frozen state). For PBX-9404, the usual CJ pressure of 37 GPa implies that γ = 2.851, while p = 34 GPa implies that γ = 3.191 and p = 33 GPa implies that γ = 3.318.

Only one experimental technique, the embedded particle velocity gauge of Hayes and Tarver,[7] has been able to yield an estimate of γ near the CJ state of detonating solid explosives. The gauge measures particle velocity as function of time and thus yields pressure versus time and volume versus time for steady waves.[7] These records are then differentiated and plotted as $\partial \ln p / \partial \ln V$ or γ. Figure 7 shows the resulting γ versus time record for detonating PBX-9404 and the corresponding γ for the standard JWL product equation of state based on $P_{CJ} = 37$ GPa. The agreement in Fig. 7 is remarkable considering the difficult environment for both experiment and theory. The experimental record also shows that γ increases just behind the CJ state as it does for the JWL equation of state. Experiments in which the gauge survives longer and measures γ to greater product expansions will hopefully be done in the near future. The γ's predicted by $P_{CJ} = 33$ or 34 GPa are obviously far too high.

Fickett's LJD equation of state calculations indicate that the frozen versus equilibrium CJ sound velocity differences are not large enough to account for all of the offset between the overdriven detonation data and the standard JWL equation of state. However, the frozen and equilibrium sound velocities may differ by larger amounts at pressures above CJ, and this should be checked for various equations of state by TIGER calculations.[22]

3. Two Other Possibilities in the Pathological Case

Two other possible explanations of some or all of the dilemma have been proposed and these involve the relative compressibilities of the unreacted explosive and its reaction products at pressures above CJ. These explanations are shown graphically in the p-V plane in Fig. 8, in which the unreacted explosive Hugoniot curve is "stiffer" than that of the products described by the standard JWL equation of state and state S' lies to the right of state P1. This type of situation has been discussed in terms of self-sustaining detonation as the "pathological case" by von Neumann,[23] in terms of a gaseous detonation with a mole decrement (less moles of products than original moles of reactants) by Fickett and Davis,[18] and in terms of porous condensed phase explosives by Tarver.[24] This situation could develop in overdriven detonations because the slope of the U_s-u_p curve for the piston-supported overdriven detonation experiments in Fig. 3 is less than one (actually ~0.8 for most of the explosives studied thus far).[21] The usual slope of an unreacted explosive Hugoniot is greater than two so these two Hugoniots eventually have to cross somewhere above the von Neumann spike pressure. This causes no particular problem in computer calculations where it occurs because the reactive flow model simply shocks up to state S' in Fig. 8 and reacts with increasing pressure to state P1 in Fig. 8. However, one might invision situations in which a pressure increase during exothermic chemical energy release is impossible and therefore the reaction would proceed in the opposite direction to state P2 in Fig. 8. An overdriven detonation experiment on such a system would thus measure state P2 as the reaction products state. While this situation has never been observed, it is a theoretical possibility. If this phenomena did occur, it might be possible to experimentally observe the discontinuous switch from the P1 product Hugoniot to the P2 Hugoniot at pressures close to point C in Fig. 8 where the P1 Hugoniot crosses the unreacted Hugoniot.

Another hypothetical situation that could occur at extremely high pressures is that the rapid exothermic chain reactions that control the energy release rates in detonation waves[24] actually slow down due to a loss of mobility of the radicals and molecules.[25] Then the state measured in a short duration piston-supported overdriven detonation experiment would actually be the unreacted (or partially reacted) Hugoniot state point S' in Fig. 8. If S' lies to the right of P1 as in Fig. 8, the unreacted Hugoniot would be mistaken for the product Hugoniot. Again this situation has never been observed but has to be mentioned as a possible explanation. Longer duration overdriven experiments and high pressure chemical kinetic studies, such as diamond anvil and thermal explosion experiments, would shed more light on the possibilities of slower energy release at extremely high pressures.

CONCLUSIONS

Four possible theoretical explanations of the observed differences between piston-supported overdriven detonation waves and the standard JWL reaction product equation of state which accurately predicts the states attained in self-sustaining CJ and converging detonation waves are discussed in detail. The simplest and most likely explanation is that additional exothermic processes occur in piston-supported waves that do not occur in self-sustaining waves. These processes have time to occur in piston-supported waves because the high pressure and temperature region is maintained by the piston motion. The effects of the additional energy release can then be communicated to the leading shock front due to the subsonic nature of the flow. In self-sustaining waves, the postulated slower exothermic processes occur in rarefaction waves, and therefore can not overtake the main reaction zone and affect detonation wave propagation. Identification of these additional exothermic processes, which may involve formation of more stable states of solid carbon and/or other reactions, is an extremely challenging experimental and theoretical problem. A second possible explanation of some of the difference involves the attainment of frozen instead of equilibrium sonic states in the very short duration piston-supported overdriven detonation experiments. Larger scale experiments are being planned to address this possibility. The other two possible explanations depend on a knowledge of the compressibilities and energy release rates of unreacted explosives at extremely high pressures and short times where experimentation has been impossible. However, high pressure static experiments, such as diamond anvil research, may eventually produce some relevant data. The experimentation on overdriven detonation waves has certainly pointed out many fascinating areas of theoretical and experimental research that are relevant to the understanding the states attained and the work done by detonating solid explosives.

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TABLE 1.
Equations of State and Reaction Rate Parameters used in the Reactive Flow Calculations

JWL parameters	Unreacted	Standard Products	Lower Pressure Products
A (Mbars)	9522	8.524	41.8548
B (Mbars)	−0.05944	0.1802	1.2553
R_1	14.1	4.6	7.7
R_2	1.41	1.3	2.4
W	0.8867	0.38	0.38
C_v (Mbars/K)	2.781×10^{-5}	1×10^{-5}	1×10^{-5}
E (Mbars-cc/cc)	8.287×10^{-3}	0.102	0.102
Yield strength (Mbars)	0.002		
Shear modulus (Mbars)	0.0454		
Von Neuman spike and CJ values			
D (mm/μs)	8.80	8.80	8.8
p (Mbars)	0.3981	0.370	0.340
ρ_o/ρ	0.7210	0.740	0.761
up (mm/μs)	2.455	2.29	2.10
Reaction rate parameters			
I (μs^{-1})	44		
G (μs^{-1} $Mbars^{-Z}$)	850		
Z	2.0		

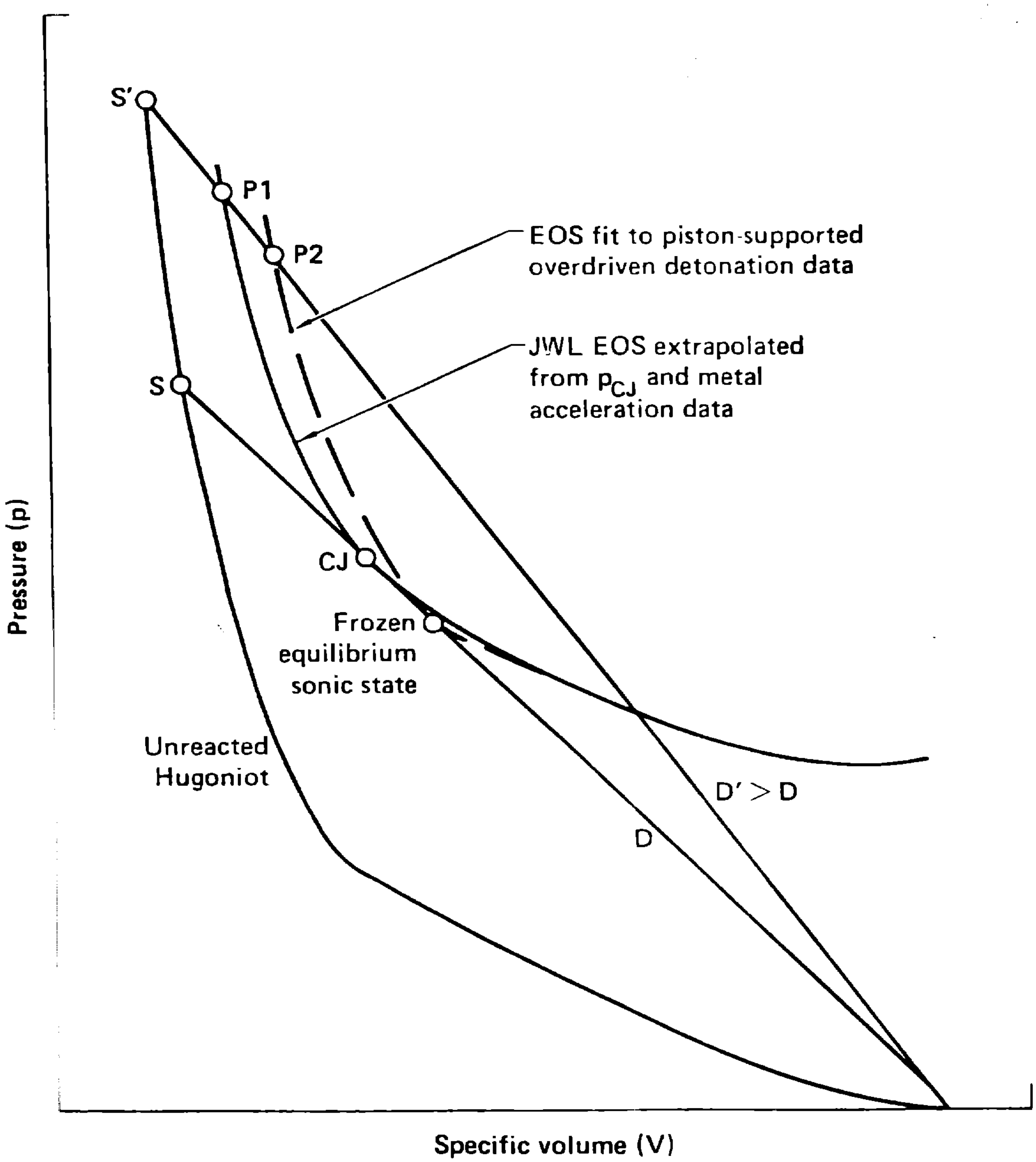

FIGURE 1.
Piston-supported overdriven detonation data compared to the standard JWL EOS in the p-V plane

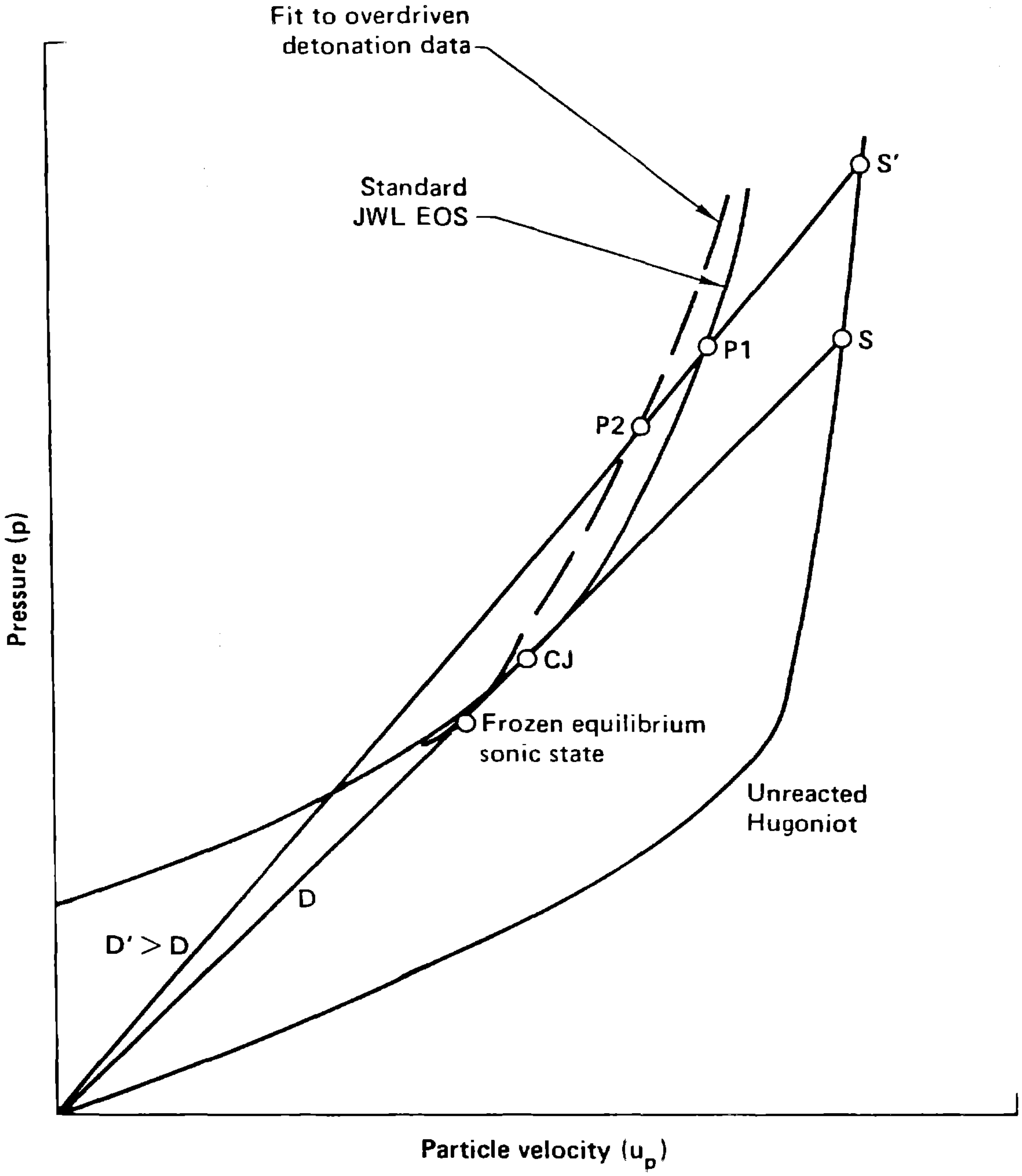

FIGURE 2.
Piston-supported overdriven detonation data compared to the standard JWL EOS in the p-u_p plane

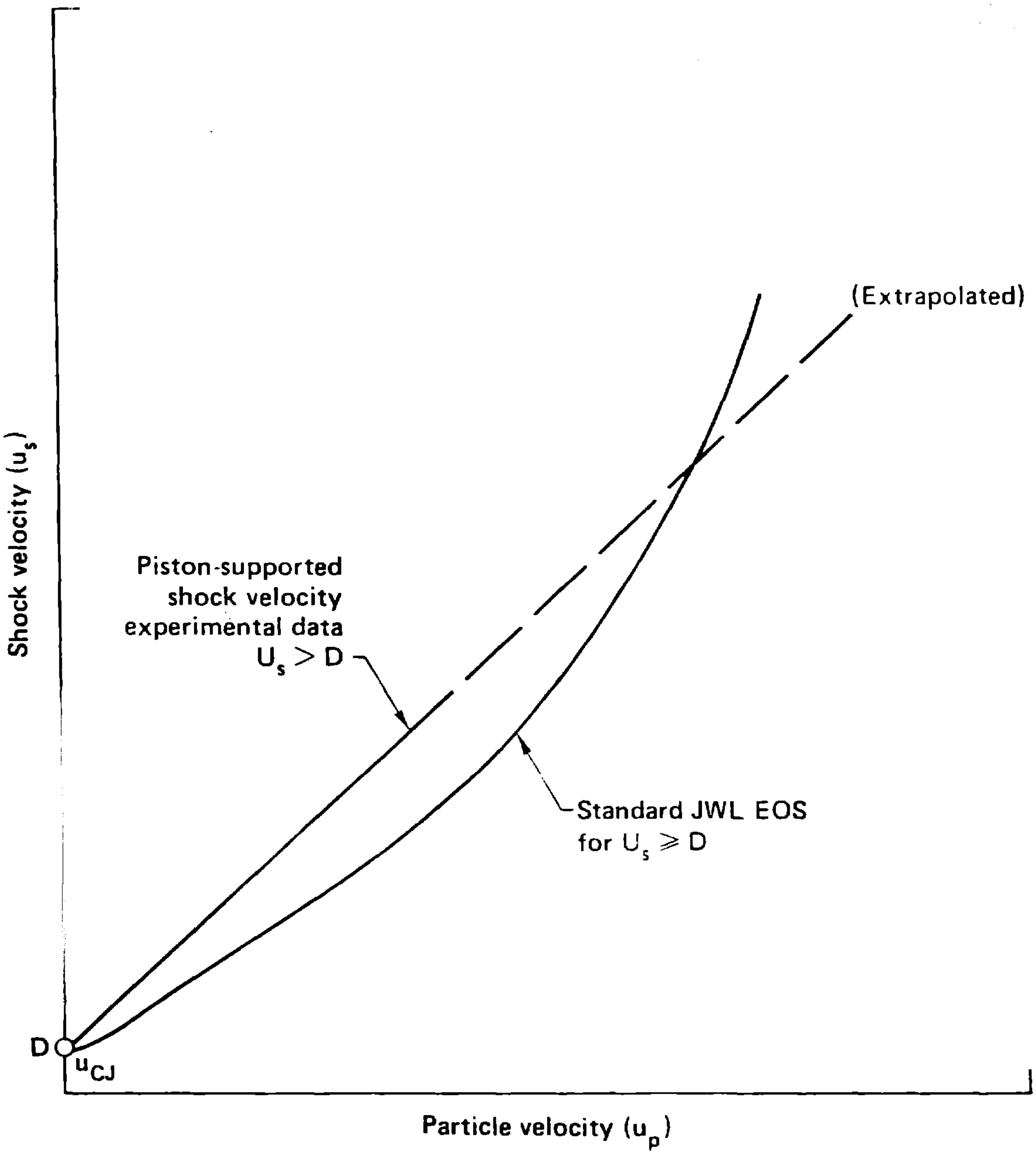

FIGURE 3.
Piston-supported overdriven detonation data compared to the standard JWL EOS in the U_s-u_p plane

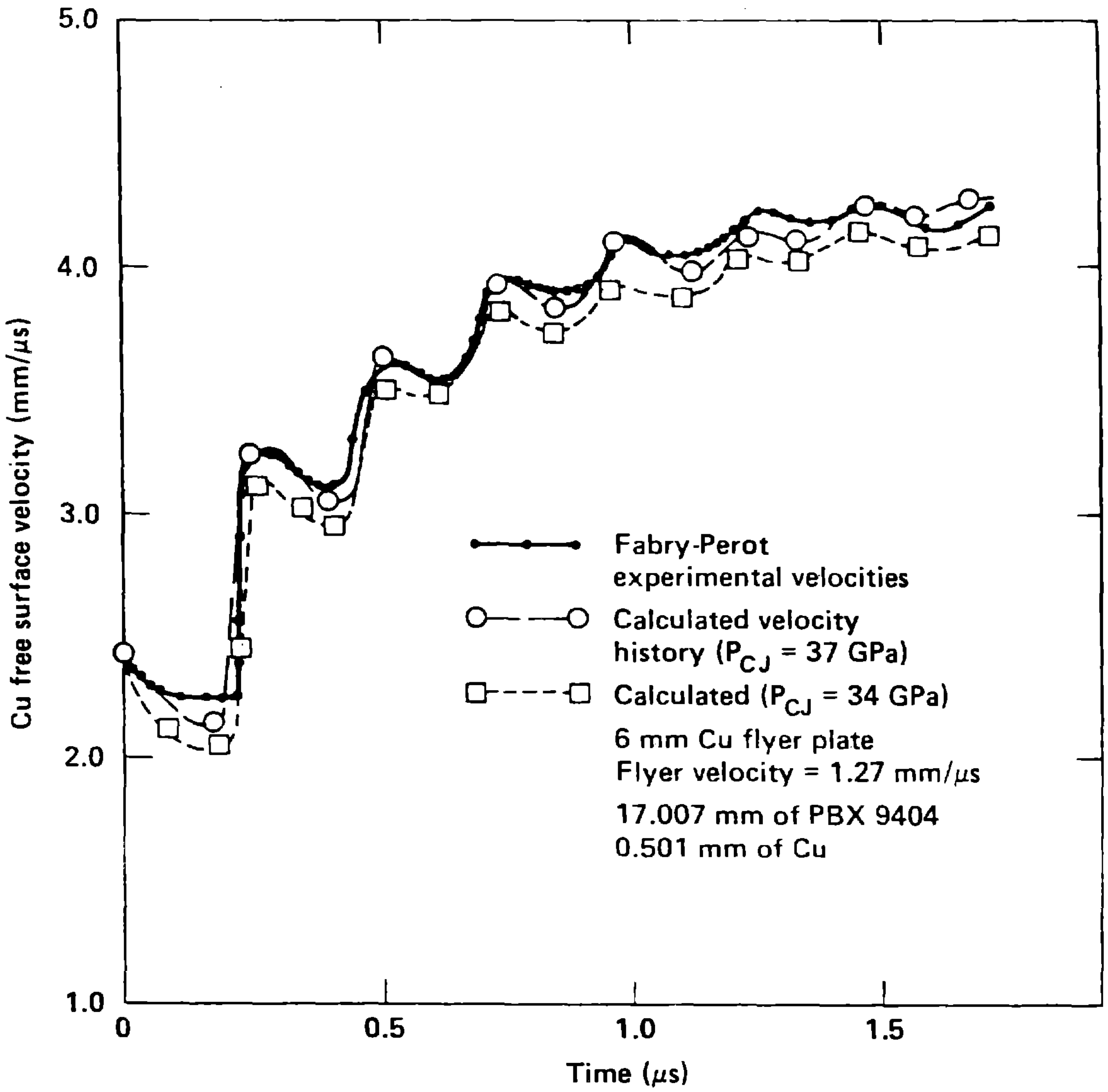

FIGURE 4.
Fabry-Perot and calculated free surface velocity histories of a 0.501 mm copper plate accelerated by detonating PBX 9404

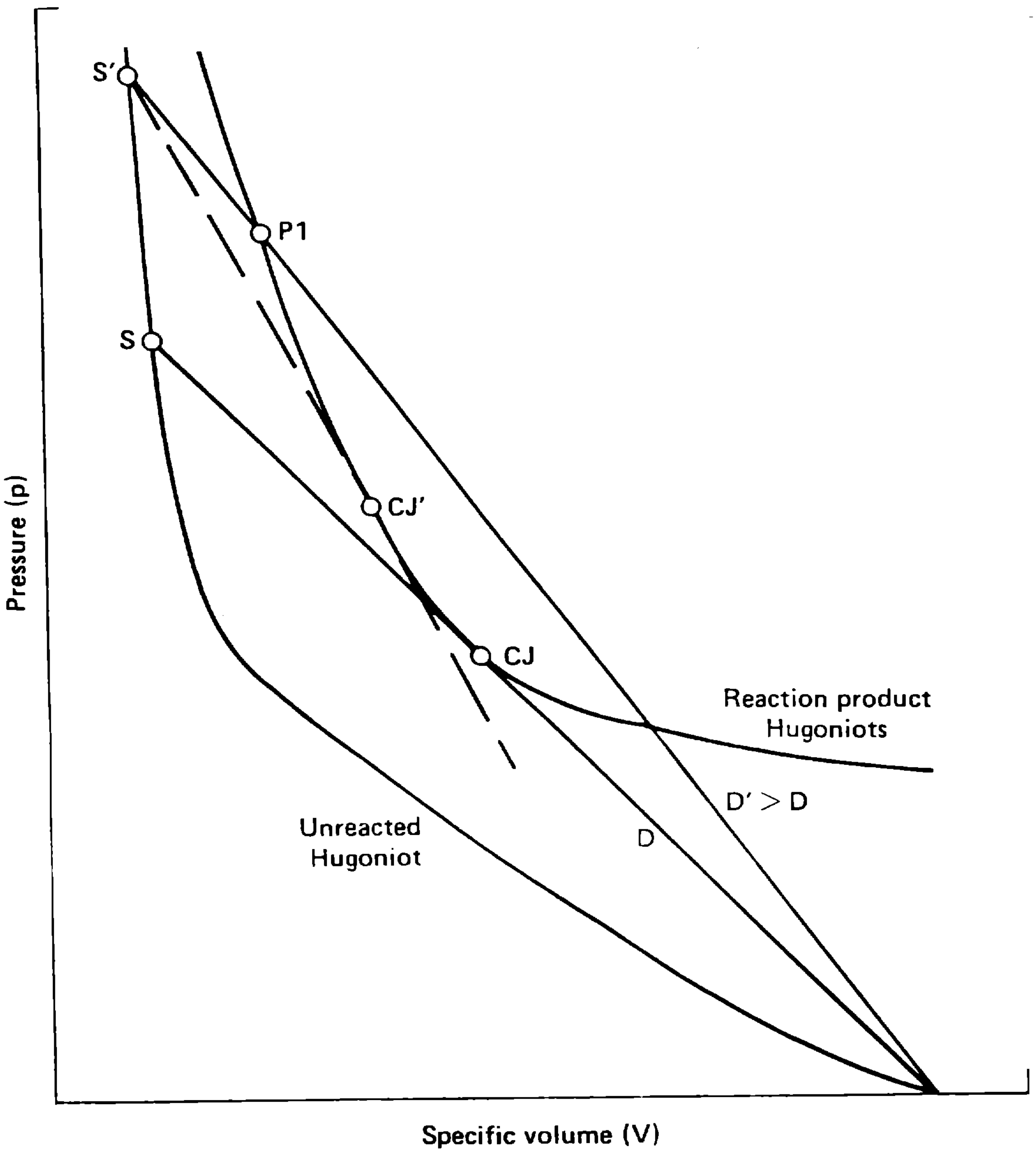

FIGURE 5.
Reaction product states for self-sustaining converging detonation waves

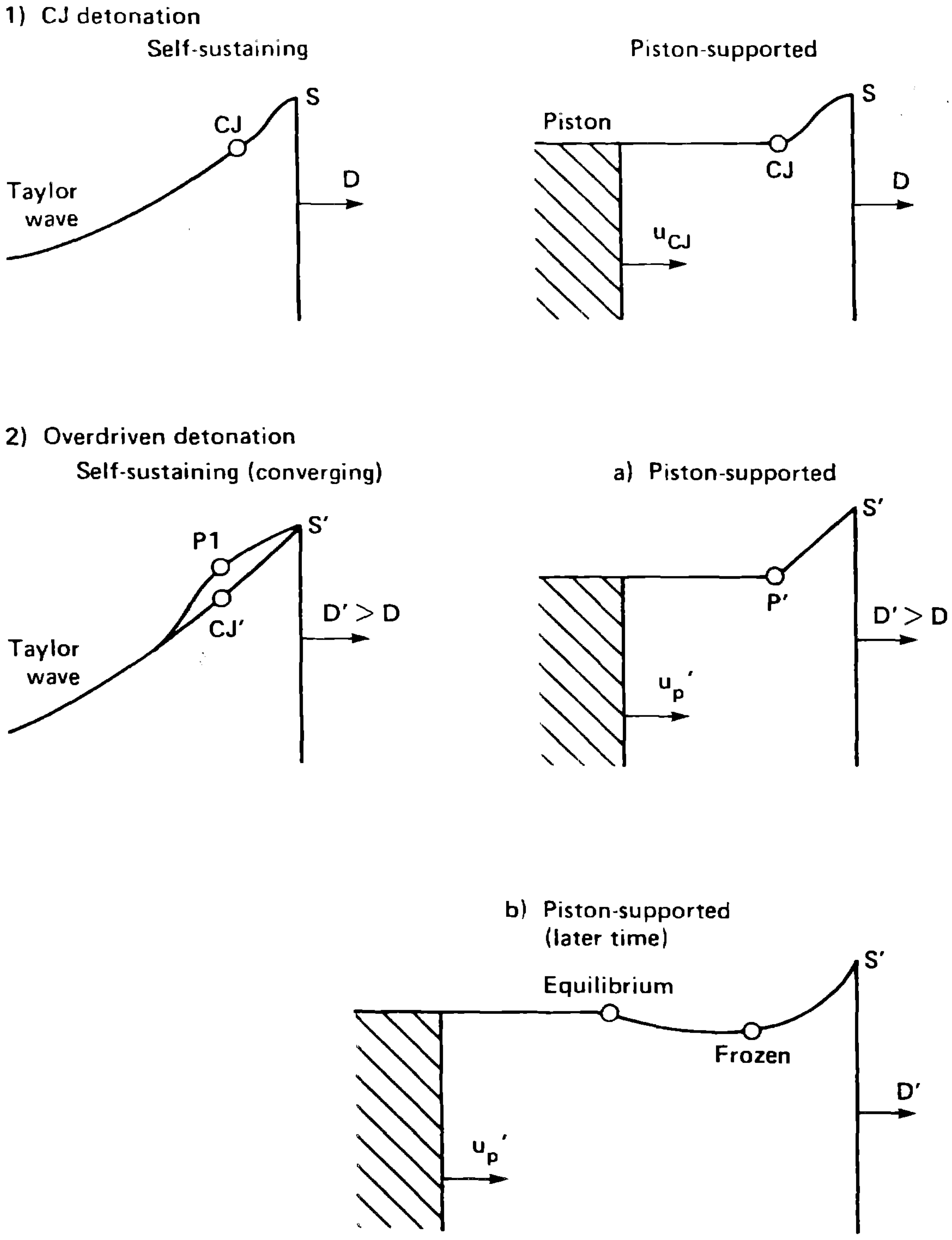

FIGURE 6.
Pressure-distance profiles for piston-supported and self-sustaining detonation waves

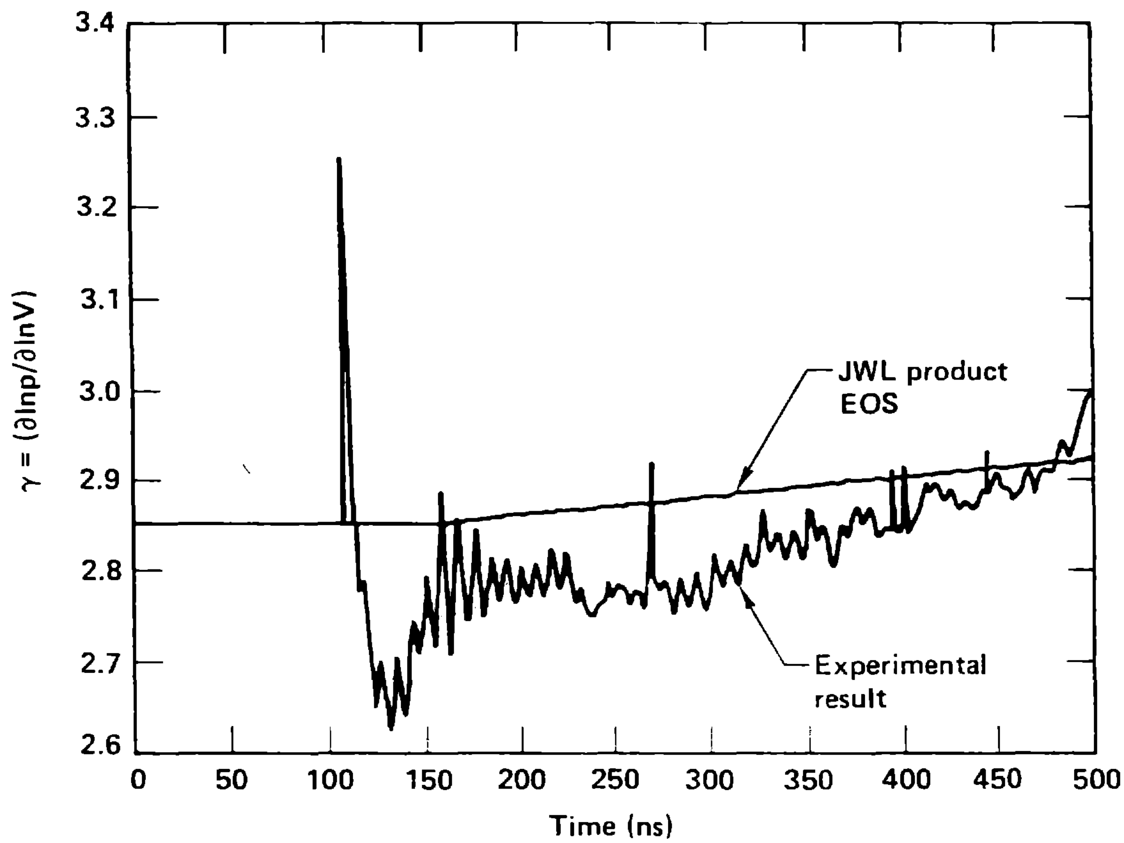

FIGURE 7.
γ derived from embedded particle velocity gauge measurement in detonating PBX-9404 compared with γ from standard JWL EOS

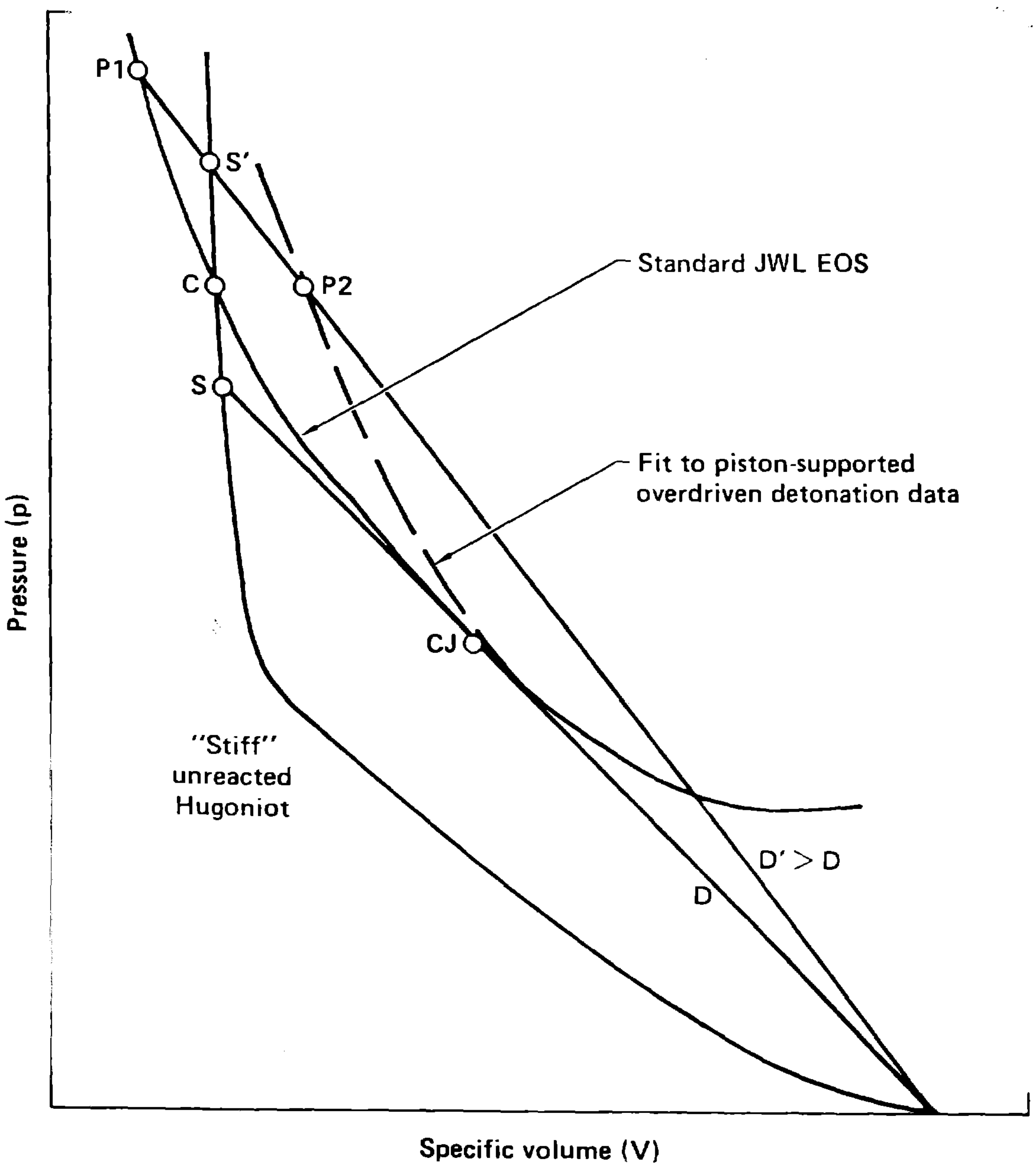

FIGURE 8.
Possible p-V states for the two "pathological" detonation cases